

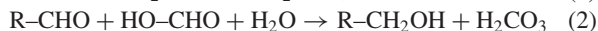
Noncatalytic Disproportionation and Decarbonylation Reactions of Benzaldehyde in Supercritical Water

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In supercritical water at 400 °C and 0.5 g/cm³ (37 MPa), benzaldehyde is decomposed into benzene and CO at a yield of 16% in 4 h; the latter is considered to be further converted into formic acid in the reaction condition. The decomposition competes against two types of disproportionation reactions. One is cross-disproportionation between benzaldehyde and formic acid, leading to the formation of benzyl alcohol and CO₂. The other is self-disproportionation of benzaldehyde where benzyl alcohol and benzoic acid are equally generated. The weight of the cross-disproportionation is larger than that of the self-disproportionation. As a result, the yield (6.6%) of benzyl alcohol is ≈2.5 times as large as that of benzoic acid.

Hot water including supercritical one attracts much attention recently as a green alternative to harmful organic solvents for chemical processes.^{1–10} To control hydrothermal reactions of a variety of organics in a earth-friendly manner, we need a systematic investigation on each functional group. Aldehydes are important in laboratorial and industrial processes as solvent and synthetic starting materials. It exhibits the Cannizzaro (disproportionation) reaction at ambient conditions; only in the presence of a large amount of base catalyst, it transforms into alcohol and acid at the ratio of 1:1.¹¹ Recently,^{3,6} we have found formaldehyde and acetaldehyde undergo two types of noncatalytic disproportionation reactions with hot water; one is the self-disproportionation between two aldehydes of the same kind, and the other is the cross-disproportionation between formic acid and formaldehyde or acetaldehyde. They are expressed as follows:



Formic acid, HO-CHO, is considered to be produced via CO generated by the thermal decarbonylation of aldehydes. Alcohol is actually yielded in excess to acid, and for the case of acetaldehyde, moreover, the cross-disproportionation is dominant in the alcohol production. The competing disproportionation reaction scheme represented by Eqs 1 and 2 is expected to be common to other aldehydes in hot water. Thus, the natural, next target to disclose the two disproportionation reactions is benzaldehyde, the simplest member of the aromatic aldehydes. Nevertheless, the competitive reaction mechanism is not yet established by previous studies on benzaldehyde.^{4,5} The key parameter, the ratio of alcohol to acid, was not determined there. The competitive disproportionation reactions are confirmed here also for benzaldehyde.

Benzaldehyde (Nacalai Co., 98%) was used without further purification. Water, used as solvent and reactant, was distilled 3 times after ion-exchanged. Benzaldehyde and water, in molar ratio 1:111, were loaded in a quartz tube of 1.5-mm i.d. No cata-

lytic effect is present for quartz. The sample was sealed after the air in the reactor was replaced by argon. It was then put into an electric furnace kept at 400 °C; the temperature was controlled within ±1 °C. In the sample vessel, the reaction system was homogeneous in supercritical water whose density was set to 0.5 g/cm³ by controlling the ratio of the sample volume to the vessel volume at room temperature. Under the reaction condition, the initial concentration of benzaldehyde corresponds to 0.25 M. After a reaction time of 4 h, the sample was removed from the furnace quickly and quenched in a cold water bath; it took less than 30 s for the sample to cool down. At this stage, the aqueous, organic, and gaseous phases coexist in the sample vessel. The aqueous and gaseous phases were separately subjected to ¹H and ¹³C NMR measurements at room temperature using ECA-400 (JEOL). A solution of 1,3,5-trioxane in D₂O was sealed in a capillary and used as an external reference. The sample was then opened and the aqueous and organic phases were recovered in a single phase in acetone-*d*₆. The acetone solution was used for the NMR measurement to quantify the products and residual benzaldehyde. For comparison, the neat pyrolysis was also examined at 400 °C. In this case, no solvent was added and the density of benzaldehyde was set to 0.25 M at 400 °C.

Figure 1 shows the proton spectrum for the aqueous phase after the reaction of 4 h. Before the reaction, three peaks assigned to benzaldehyde were detected; the peaks at 7.59, 7.73, and 7.92 ppm represent meta, para, and ortho protons of the phenyl ring, respectively. After the reaction, new peaks of benzyl alcohol (7.31–7.43 ppm), benzoic acid (7.50, 7.64, and 7.98), and benzene (7.40 ppm) emerged. Toluene was also detected as a minor product at 2.22 ppm for the methyl proton. The production of benzyl alcohol and benzoic acid indicates that the self-disproportionation reaction of benzaldehyde takes place without catalyst in supercritical water. In Table 1, we summarize the yields of the products. The conversion of benzaldehyde is ≈40%, and the main product is benzene. It should be noted that the yield of benzyl alcohol is ≈2.5 times as large as that of benzoic acid, although the alcohol/acid ratio by the self-disproportionation reaction is 1. This implies that benzyl alcohol production involves

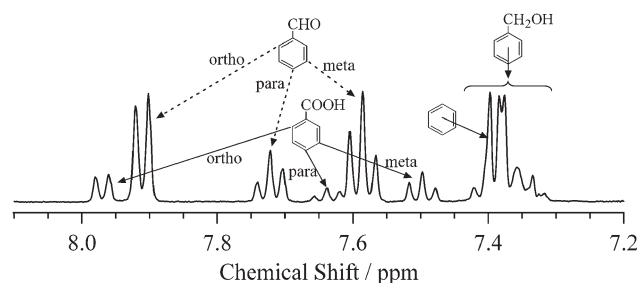


Figure 1. The liquid-phase ¹H spectrum for the products of benzaldehyde reaction for 4 h at 400 °C and a water density of 0.5 g/cm³.

Table 1. Product yields of benzaldehyde reaction without and with HCOOH addition; 400 °C, reaction time of 4 h, and $[\text{Ph-CHO}]_0 = 0.25 \text{ M}$

Products	Yield/%	
	HCOOH not added	HCOOH added ^a
Ph-CHO	61.7	42.1
Ph-CH ₂ OH	6.6	10.3
Ph-COOH	2.6	1.5
Ph-H	15.8	13.5
Ph-CH ₃	0.3	2.7
H ₂	≈7	≈112

^aThe concentration of added HCOOH is 0.25 M at initial condition.

another reaction pathway in addition to the self-disproportionation of benzaldehyde.

Figures 2a and 2b illustrate the proton and carbon spectra for the gas phase of the reacted system, respectively. In Figure 2c, the carbon spectrum for the neat pyrolysis products of benzaldehyde at 400 °C is shown. When no solvent water is added, only benzene and CO are produced equally by the decarbonylation reaction. In supercritical water, in contrast, H₂ and CO₂ were detected in Figures 2a and 2b and CO was not within our precision. In a separate experiment, we confirmed that benzoic acid was stable in the present experimental condition. In other words, neither benzene nor CO₂ are produced by the decarboxylation of benzoic acid. The benzene production thus arises exclusively from the decarbonylation of benzaldehyde; as referred to in Table 1, the decomposition to benzene and CO is dominant in supercritical water. This suggests that the CO generated through the decarbonylation is further converted by a reaction with water to formic acid.⁶ As shown in the previous communications, formic acid reduces formaldehyde and acetaldehyde to methanol and ethanol, respectively, and is itself oxidized to carbon dioxide and H₂O.^{3,6} This is the cross-disproportionation with formic acid, the hydroxyl "aldehyde". As can be seen in Table 1, the yield of benzyl alcohol is ≈2.5 times larger than that of benzoic

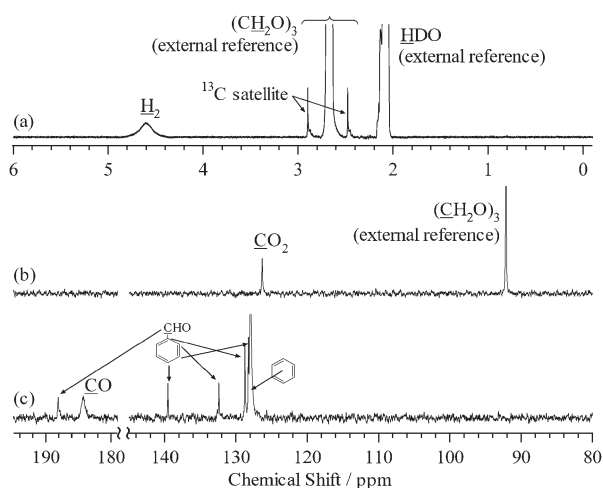


Figure 2. The gas-phase spectra at a reaction time of 4 h for benzaldehyde. (a) and (b) represent the ¹H and ¹³C spectra, respectively, for the reaction in water at 400 °C and 0.5 g/cm³, and (c) stands for the ¹³C spectrum taken at 180 °C for the pyrolysis at 400 °C without solvent. The external reference employed is 1,3,5-trioxane in D₂O, and the magnetic susceptibility is corrected.

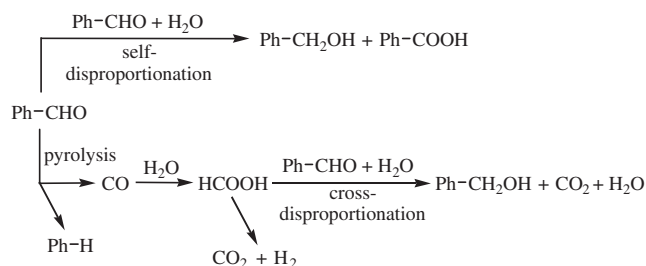


Figure 3. Reaction pathways of benzaldehyde in supercritical water.

acid. This is a clear indication of the larger contribution of the cross-disproportionation than that of the self-disproportionation.

The importance of the cross-disproportionation is confirmed by the increase in the yield of benzyl alcohol induced by the excess addition of formic acid. The addition of formic acid of 0.25 M increased the production ratio of alcohol/acid to ≈7 from ≈2.5. This means that formic acid acts as a reducing reagent to benzaldehyde. Thus, it is explained that the excess benzyl alcohol in Figure 1 is generated through the cross-disproportionation reaction between benzaldehyde and formic acid as represented by Eq 2. On the other hand, H₂ is formed by the independent decarboxylation reaction of formic acid.¹⁰ In conclusion, the reaction pathways of benzaldehyde in supercritical water in the absence of catalyst can be shown in Figure 3.

Although the reaction of benzaldehyde in supercritical water has ever been examined, there exist discrepancies with respect to the reaction products and pathways. Funazukuri et al.⁴ reported such products as benzyl alcohol, toluene, and benzene without detecting benzoic acid and assumed the presence of CO. Ikushima et al.⁵ considered only the self-disproportionation. In this communication, we have demonstrated that benzaldehyde exhibits the decarbonylation and two types of disproportionation reactions in supercritical water.

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